

Electron Localization in a Mixed-Valent (+2/+3) Di-Iron Complex

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Mixed-valence coordination complexes are molecules containing at least two of the same metal ions, where the formal oxidation state (charge) of the metal ions is different. Such complexes are of interest to inorganic chemists because of their unusual electronic and magnetic properties. An average (sometimes non-integral) charge may be the best assignment for the oxidation state due to the delocalization of electrons, such that the charge at each metal ion is effectively the same value. Accurate determination of bond lengths can be used to assess the extent of electronic delocalization. X-ray absorption spectroscopy (XAS) performed at the NSLS was used to determine that a mixed-valence complex with a $\text{Fe}_2(\text{OH})_2$ core is best described as a complex with one Fe^{2+} and one Fe^{3+} ion. The XAS results were used along with X-ray diffraction to determine the crystal structure.



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Dinuclear iron complexes containing a Fe_2O_2 rhombic core (top right) are of interest as models of the structure and function of the active site of the class of non-heme iron enzymes to which the hydroxylation protein of methane monooxygenase (MMOH) belongs. This enzyme is responsible for the bacterial conversion of methane to methanol. Recently, a mixed valence ($\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}$) form of MMOH was structurally characterized as containing a triply-protonated rhombic core (i.e. one $\mu\text{-OH}$ and one $\mu\text{-OH}_2$ bridging between the iron atoms). [Wittington, D. A. and Lippard, S. J., *J. Am. Chem. Soc.*, 2001, 123, 827-838.] While synthetic $\text{Fe}_2\text{O}_2(\text{H})_{0.2}$ compounds with a rhombic core exist for the II-II, III-III, III-IV oxidation states, the II-III state was unknown.

Using the neutral capping ligand, *N,N'*-dimethyl-*N,N'*-bis(2-pyridylmethyl)ethane-1,2-diamine (L) (top right), to complete the coordination requirements of the iron atoms, and thus prevent an uncontrolled polymerization to form iron(III) hydroxides, we prepared and crystallized the first example of a synthetic diiron complex in the II-III iron oxidation state and containing a rhombic core. The compound, $[\text{L}_2\text{Fe}_2(\text{OH})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, is unstable in solution. In the solid state, crystals decompose in weeks. The products of decomposition are iron (III) compounds. The initial structure of $[\text{L}_2\text{Fe}_2(\text{OH})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, determined by single crystal X-ray diffraction, showed that the two iron atoms were related by symmetry, suggesting a delocalized mixed-valence complex ($\text{Fe}^{+2.5}\text{Fe}^{+2.5}$) with an average Fe-O distance of 1.98 Å. All other things being equal, the metal-donor distances depend on metal oxidation state and are shorter for higher oxidation states. Given the chemical similarity of the local environment of each iron atom of the molecule, identical oxidation states (of +2.5) seemed plausible. The physical interpretation of such a non-integer oxidation state is that there is little barrier for electron transfer between the metal ions. However, an alternative explanation is that the compound can be regarded as a valence trapped $\text{Fe}^{\text{II}}\text{-Fe}^{\text{III}}$ compound and the crystal structure is disordered.

In experiments performed at beamline X18B at the NSLS, we found that structural disorder in the crystal lattice is indeed the cause of the apparent equivalent oxidation states. The best fit of the X-ray absorp-

tion fine structure (XAFS) measurements was obtained by refining 2 Fe-O distances each to 1.90 ± 0.03 and 2.12 ± 0.08 Å rather than using the Fe-O distance found in the crystal structure (**Figure 1**). The refined Debye-Waller factor (σ^2) for these Fe-O shells was 0.004 Å², typical of what is found for compounds with only vibrational disorder in the bond lengths. The iron K-edge (XANES) spectrum could be well modeled as arising from 50% Fe²⁺ and 50% Fe³⁺ (**Figure 2**). The combined results from XANES and EXAFS analysis indicate that the iron atoms in $[\text{L}_2\text{Fe}_2(\text{OH})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ are localized in their valence state on the X-ray time scale. Since the same time scale applies to X-ray diffraction, the apparent equivalence in Fe-O bond lengths in the crystal structure is ascribed to packing disorder.

Based on these results, the single crystal diffraction data of $[\text{L}_2\text{Fe}_2(\text{OH})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ were re-fit using two half-occupancy isotropic oxygen atoms instead of the single anisotropic bridging oxygen atom (**Figure 3**). The two models fit the diffraction data equally well ($R_w = 0.044$) but the disordered model is obviously preferred because it explains the EXAFS and XANES results. In the disordered model, the averaged distances ascribed to Fe^{III}-O (1.89 Å) and to Fe^{II}-O (2.07 Å), as well as the Fe-Fe distance (2.95 Å), are within the uncertainty ranges for these parameters established by EXAFS analysis. These results show that, despite an ostensibly symmetrical chemical environment for both iron atoms of $[\text{L}_2\text{Fe}_2(\text{OH})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, the electrons localize such that one Fe^{II} and one Fe^{III} are present in the complex.

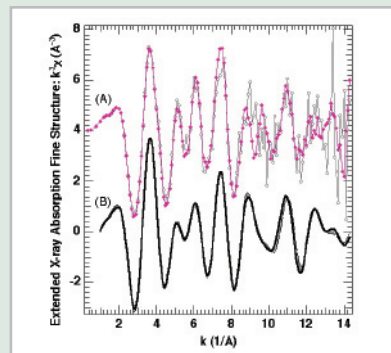
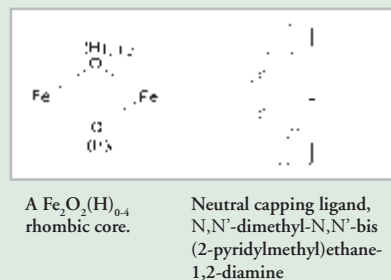


Figure 1. EXAFS analysis of $[\text{L}_2\text{Fe}_2(\text{OH})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$. (A) The fluorescence (circles) and transmission (diamond) detected EXAFS are compared (both are offset by $+4$ Å⁻³; no systematic difference are evident). (B) Fourier filtered EXAFS (thick line) and simulation of the EXAFS to determine Fe-X distances discussed in this article.

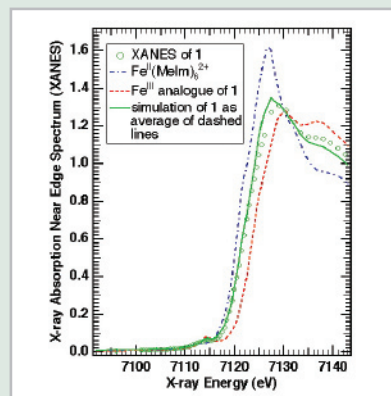


Figure 2. XANES of $[\text{L}_2\text{Fe}_2(\text{OH})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$ and its simulation representing contributions of 50% from Fe^{II} and 50% from Fe^{III} XANES shapes.

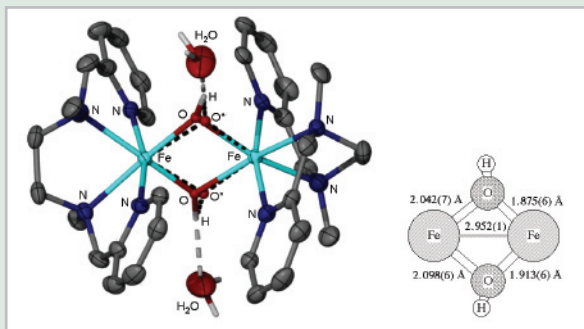


Figure 3. X-ray crystal structure of the cation $[\text{L}_2\text{Fe}_2(\text{OH})_2](\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$, with enlarged geometry of the $\text{Fe}_2\text{O}_2\text{H}_2$ rhombic core inferred from a combination of XAS and X-ray diffraction experiments.